Article

Resonant Light Scattering: from Diatomic Molecules to Laser-Trapped Microparticles

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Dedicated to the 70th anniversary of Professor Dr. Oswaldo Sala

Received: June 17, 1996

São discutidas aqui investigações recentes, experimentais e teóricas, em espalhamento Raman linear e não linear ressonantes para diferentes sistemas, executados em laboratórios do autor. Primeiramente apresentados os estudos do espalhamento Raman ressonante contínuo de moléculas de halogênio e inter-halogênios, onde mostramos como os experimentos podem ser simulados aplicando-se tanto a teoria independente como a dependente do tempo. A determinação precisa de funções de onda e estados excitados repulsivos, tempos de relaxação de espalhamento, bem como dos princípios de reflexão e simetria são discutidos. Na sequência, apresentamos os resultados das espectroscopias de absorção, Raman ressonante e de espalhamento Raman anti-Stokes coerente (CARS) para monocristais de diacetileno parcialmente polimerizado. São investigadas as propriedades eletrônicas e estruturais dos poliacetilenos que resultam em efeitos de cromismo. A seguir, passamos a discutir ressonâncias dependentes da morfologia, observadas nos espectros Raman de microgotas sob levitação óptica. Uma simulação teórica de espectros Raman-Mie permite a atribuição destas ressonâncias dependentes da morfologia e de suas mudanças de posição espectral com o tempo. Finalmente, mostramos como esta técnica pode ser usada para acompanhar reações químicas em uma simples micropartícula aprisionada por laser.

Recent experimental and theoretical investigations of linear and nonlinear resonance Raman scattering in different systems performed in the authors's laboratories are discussed. We first report on studies of continuum resonance Raman scattering in halogen and interhalogen molecules, where we show how the experiments can be simulated applying time-independent as well as time-dependent theory. Precise determinations of repulsive excited state functions, scattering delay times, and a reflection and a symmetry principle are discussed as well. Next, we report on absorption, resonance Raman, and resonance coherent anti-Stokes Raman scattering (CARS) spectroscopy in partially polymerized diacetylene single crystals. Electronic and structural properties of the polydiacetylenes which lead to chromism effects are investigated. Then we discuss morphology-dependent resonances observed in the Raman spectra of optically levitated microdroplets. A theoretical simulation of the Raman-Mie spectra allows the assignment of the observed morphology-dependent resonances and their changes in spectral position with time. We show how this technique can be used to follow chemical reactions in single laser-trapped microparticles.

Keywords: *resonance Raman scattering, CARS, continuum resonance Raman spectroscopy, halogens, interhalogens, diacetylenes, polydiacetylenes, Raman-Mie-scattering, morphology dependent resonances, time-dependent theory, scattering delay times, reflection principle, symmetry principle*

Introduction

Since its discovery in 1928¹, Raman scattering has become a valuable and wide-spread tool for the spectro-

scopic investigation of many kinds of interesting systems. In the present paper we review some of the work performed on this subject in our laboratories. We particularly concentrate on Raman excitation in resonance with electronic

states, as well as on so-called Raman-Mie scattering where in addition to the Raman bands, morphology-dependent resonances can be observed.

First, we report on investigations of simple, diatomic systems where resonance takes place with the continua of repulsive electronic states. Continuum resonance Raman scattering, first observed by Holzer *et al.*² in 1970 on various halogen and interhalogen gases, has been a topic of experimental and theoretical interest for some time³⁻⁶. First approaches to describe Raman scattering from molecules theoretically started with the derivation of the famous dispersion relationship by Kramers and Heisenberg⁷, and by Dirac⁸ using time-dependent perturbation theory. Since continuous excited electronic states are mainly responsible for the intensities in this type of inelastic scattering, it is possible to derive the exact form and position of the repulsive part of the excited state potential functions by comparing calculated with experimentally recorded spectra. For this purpose we developed computing programs including extensive fitting routines which allow the exact simulation of the continuum resonance Raman spectra of simple systems within acceptable computing times. In this regard, new work has recently been carried out in our research group for the isotopically pure molecules ¹²⁷I₂ (Ref. 9), ⁷⁹Br₂ (Ref. 10), ³⁵Cl₂ (Ref. 11), ¹²⁷I³⁵Cl (Refs. 12, 13), ¹²⁷I⁷⁹Br (Refs. 14, 15), and ⁷⁹Br³⁵Cl (Ref. 16).

Resonance Raman spectra carry information about nuclear as well as electronic dynamics, usually on a femto-second time scale. The best way to intuitively understand the dynamic sources of such spectra is through time-dependent quantum mechanics. The time-dependent theory for describing resonance Raman scattering was mainly developed by Heller and coworkers over a decade ago^{17,18}. Equivalent to the conventional energy frame Kramers-Heisenberg-Dirac (KHD) formulation^{7,8}, it is free from any approximation, except for the usual second order perturbation method used to derive the KHD expression. The time dependent formulation lends itself to an interpretation where localized wave packets follow classic-like paths.

In this paper we report on experimental and theoretical studies of continuum resonance Raman scattering in isotopically pure halogen and interhalogen molecules. We explicitly show how the observed spectra can be simulated applying the time-independent as well as the time-dependent theory. Precise determinations of repulsive excited state functions, scattering delay times, and a reflection and a symmetry principle are discussed as well.

The resonance Raman technique also allows the investigation of more complicated molecular systems, such as diacetylene polymers (PDAs). Due to their nonlinear properties, diacetylene polymers are candidates for future applications in optoelectronics or molecular electronics¹⁹. The large third-order nonlinear optical response in PDA crystals was first reported by Sauteret *et al.*²⁰. The third-or-

der susceptibilities, $\chi^{(3)}$, of the polymerized crystals reach values comparable to those of inorganic semiconductors. Particular properties of these polymers are the reversible and irreversible color changes of various kinds, known as thermochromism²¹⁻²⁴, solvatochromism²⁵⁻²⁶, photochromism²⁷, and other forms such as pressure-induced chromism²⁸. These chromisms lead to changes in the absorption as well as in the Raman spectra. Though a number of extensive studies have been carried out, the molecular mechanism giving rise to the chromic transition is still a controversial subject. The key to this problem seems to be connected to the understanding of the sensitivity of the electronic properties to polymer backbone conformation.

Upon thermal annealing or exposure to high energy radiation diacetylene monomers (DAs) undergo a topochemical solid state polymerization²⁹. From this reaction, polymer chains are formed which have a substantial π electron delocalization, forming a pseudo-one-dimensional electronic system. The extended conjugated π bond structure can be described by two resonance forms. The mesomeric structures are called the acetylenic ($=RC-C\equiv C-CR'=$)_n and the butatrienic ($-RC=C=C-CR'-$)_n structures.

Suppositions that a change between the two mesomeric structures causes the observed color changes³⁰ have been put in doubt by recent experimental and theoretical results³¹. The assumption that interruptions of the conjugation length are the true reason for color effects arose relatively early³², and is the most accepted one at this point in time. Such interruptions could be caused by configurational or chemical defects. Transitions from a planar to a nonplanar form of the PDA chain explain shifts to higher energies in the absorption spectrum. The planar-nonplanar conformational change in the backbone results in a shorter conjugation length. In this context, an essential influence of the sidegroups has been proven by experiments²¹, as well as by theoretical considerations³¹.

A special form of chromism was recently introduced³³. In the reddish monomer crystals of the DAs TS6, FBS, and TS/FBS (see Table 1), sharply separated yellow-colored zones were observed. These color zones show a blue-shifted absorption (Y absorption) in addition to the normal red absorption. The red absorption (P absorption) results from polymer chains which originate during crystal growth. The TS6, FBS, and TS/FBS crystals are single crystals in which all polymer chains lie parallel to the *b* axis of the crystal. A typical appearance of color zones is

Table 1. Substituents of diacetylenes (TS6, FBS, TS/FBS).

Diacetylene	Substituent
FBS	$R = R' : -CH_2-O-SO_2-$ $-F$
TS6	$R = R' : -CH_2-O-SO_2-$ $-CH_3$
TS/FBS	$R \equiv TS6 \quad R' \equiv FBS$

presented in Fig. 1, together with the axes of the monoclinic crystal lattice.

The color zones in these DAs have already been characterized by absorption and luminescence spectroscopy³³. The aim of the present work is a more accurate investigation of the observed chromism by making use of several optical spectroscopic methods. We believe that by these methods more evidence of the electronic and structural nature can be gained. Here, we present experimental results from absorption, luminescence, resonance Raman, and resonance CARS (coherent anti-Stokes Raman scattering) measurements and we compare our results with those obtained for other types of chromism. A theoretical interpretation by means of Franck-Condon calculations is presented elsewhere^{34,35}. In this contribution we also show some of the results from the simulations based on the theoretical model.

Finally, applications of Raman scattering to optically levitated microdroplets are also presented. In the past twenty years, micrometer-sized solid and liquid particles have been extensively studied because of their growing significance in atmospheric and environmental science, combustion chemistry, medicine and biology³⁶⁻⁴⁵. The microparticle properties under investigation include the determination of the size, shape, refractive index, temperature, and evaporation and condensation behavior of homogeneous or mixture droplets⁴⁶⁻⁵⁰, as well as the chemical composition, reactions and interaction and exchange phenomena at the droplet interface⁵¹⁻⁵⁴.

Linear and nonlinear optical processes like Raman scattering, stimulated Raman scattering (SRS), coherent anti-Stokes Raman scattering (CARS), fluorescence and lasing, in conjunction with innovations in the fields of laser techniques and single particle traps based on electro-dynamic or optical forces, have led to many new techniques for microparticle investigation⁵⁵⁻⁵⁹. In addition, the combination of single particle traps with light scattering provides a non-intrusive technique for investigating individual microparticles.

Figure 1. Schematic form of diacetylene single crystals showing color zones. The speckled areas show a typical shape of the yellow color zone (Y zone).

In the case of spheres and spheroids, the particle acts as an optical cavity with well-defined resonance frequencies. Those eigenfrequencies, which depend only on particle shape, size and refractive index ratio between the inside and the outside of the particle, are referred to as Morphology-Dependent Resonances (MDRs). MDRs result whenever the injected light frequency in the particle coincides with a particular cavity mode. The internal light travels inside the droplet rim trapped by nearly total internal reflection, and forms a standing wave if the circulating wave closes in on itself in phase after one round trip. The theoretical formalism describing the internal and external scattered fields by solving Maxwell's equations was first performed by Mie in 1908⁶⁰.

In this paper we discuss how MDRs in combination with Raman and Mie scattering, can be used as a powerful diagnostic technique for the investigation of the physical and chemical properties of microparticles⁶¹⁻⁷⁰. We start with a description of an experimental setup which allows a single microdroplet to be investigated using an optical levitation technique⁷¹⁻⁷⁹. After a brief review of the Raman-Mie theory⁸⁰⁻⁸², we describe how the Raman-Mie⁶¹ spectra can be used for the determination of particle size and refractive index by experimentally matching observed MDRs with theoretically calculated MDRs⁸³. The obtained time-dependent radius and refractive index characterizes the evaporation behavior of the microdroplet under investigation. These results can be verified by calculating both the Raman-Mie spectra and the laser power that had been exerted on the particle for stable optical levitation^{78,83-87}.

We also discuss how the time-dependent radius and refractive index can be used to analyze the surface temperature of the droplet^{79,88}. Finally, we describe with two experiments the application of the experimental techniques and the theoretical formalism to complex chemical reactions. The first is an acid/base reaction occurring on the droplet surface between a capric acid/heptanol droplet and gaseous ammonia⁵⁴. The second is the radical polymerization and copolymerization reaction of styrene and single unsaturated polyester resin droplets⁸⁹.

Experimental

Continuum resonance Raman spectroscopy

The Raman spectra were recorded with a conventional 90° scattering arrangement using a Spectra-Physics Model 2085 Beam Lok argon ion laser. The laser light was focused into the sample cell with an $f = 40$ mm quartz lens. The scattered light was collected with an $f = 50$ mm (1:0.7) photo objective (for excitation with $\lambda_{\text{exc}} \geq 400$ nm), or an $f = 50$ mm (1:1.3) quartz lens (for excitation below 400 nm), and analyzed with a Spex 1404 double monochromator (gratings with 2400 lines/mm). The spectral resolution applied in these studies was between 0.6 and 1.5 cm^{-1} . The

dispersed Raman stray light was detected with a Photometrics model RDS 200 CCD Raman detection system using the scanning multichannel technique (SMT)⁹⁰. All spectra shown in this paper are original data without the application of any smoothing routines.

Scattering experiments were made on the isotopically pure (ca. 99%) molecules $^{79}\text{Br}_2$, $^{35}\text{Cl}_2$, $^{127}\text{I}_2$, $^{127}\text{I}^{79}\text{Br}$, $^{127}\text{I}^{35}\text{Cl}$, and $^{79}\text{Br}^{35}\text{Cl}$. The vapors were prepared from Na^{79}Br , Na^{35}Cl and $^{127}\text{I}_2$, respectively.

One-, two-, and four-photon spectroscopy on polydiacetylenes

The synthesis of the TS/FBS DA was performed according to Strohriegel⁹¹ and Bertault⁹², while the TS6 and FBS DAs were prepared by the method described by Wegner²⁹. The lozenged monoclinic crystals were obtained from solution and had less than 1% polymer content. The freshly grown DA crystals were cleaved parallel to the {100} surface (containing *b* and *c* axes, see Fig. 1). The resulting thin platelets were about 50 μm thick and about 3 mm long in the chain direction ($\parallel$ *b* axis). After cleaving, the DA crystals were put into a cryostat and cooled to about 10 K. Cooling of the crystals was necessary because of the enormous heat sensitivity of the DA single crystals. The polarization of light was chosen to be parallel to the *b* axis. This was required due to the high optical anisotropy of the DA crystals caused by the parallel polymer chains.

The experimental setup used for absorption and luminescence spectroscopy has been described elsewhere³³. For resonance Raman spectroscopy we used a micro Raman setup⁹³. We chose a backscattering arrangement where the incident laser light was parallel to the {100} surface of the crystal. For the detection, an OMA detector was used which allowed us to take large parts of the spectra at one time. The setup for the pulsed solid state CARS measurements has also been described elsewhere in detail⁹⁴. The simultaneous use of two dye lasers enabled us to perform scans of the Stokes laser frequency, ν_{St} , as well as the pump frequency, ν_{pu} . Therefore, resonance CARS spectroscopy was possible. The beam of the pump laser was vertically aligned to the {100} plane of the DA crystal. In order to excite specific phonons in the single crystals, the phase matching condition had to be fulfilled. This means that the difference between the pump and Stokes beam wave vector had to coincide with the wave vector of the coherently excited phonons in the crystals. This was achieved by changing the crossing angle between the pump and the Stokes beam, as well as the orientation of the plane spanned by pump and Stokes beam, relative to the crystal *b* axis.

Before each Raman or CARS measurement we took an absorption spectrum of the P and Y zone. In all experiments a strict separation of P and Y zones of the TS/FBS DA crystals was obtained by cleaving the crystals, or by appropriate

shielding of the P or Y zone. More details of the experimental part of our work are given in the Polydiacetylenes section, together with the results from the spectroscopic measurements.

Raman-Mie scattering on microdroplets

The experimental setup⁷⁷⁻⁷⁹ is schematically displayed in Fig. 2. The 514 nm line of an argon ion laser (AL) is simultaneously used for both the optical levitation of a single microdroplet and the excitation of Raman scattering. The laser plasma lines are removed by an interference filter (IF). The incident laser beam is loosely focused into the observation chamber by an 80 mm focal length lens (L1). The beam waist was chosen to be at least 3 times wider than the levitated microdroplet. Hence, the plane wave approximation is valid for all calculations. The droplets are produced by a newly developed droplet generator⁹⁵. The Raman light is collected by the microscope objective (L2), focused onto the entrance slits of a Dilor-XY Raman triple monochromator (FO, SP), and detected by use of a Peltier cooled intensified diode array (OM). The elastically scattered light is collected by the microscope objective (L4), and divided into two beams by use of a beam splitter. A photodiode (PD1) monitors the intensity from one beam. The other beam is focused onto a pair of photodiodes (PD2) which are separated from each other by a 50 μm gap. A feedback circuit (PI) connected to the remote control of the power supply and PD2 automatically adjusts the output laser power to keep the microparticle in the same horizontal position even if the droplet evaporates or undergoes an input resonance. All data, the Raman spectra, the elastic scattering, as well as the laser power, are stored in the computer.

Figure 2. Experimental setup for stable trapping of optically levitated microdroplets: L1-L4 lenses, M1-M4 mirrors, IF interference filter, Ar argon ion laser, PD1, PD2 photo diodes, FO foremonochromator, SP spectrograph, OM optical multichannel analyzer, PI proportional integral feedback system, AD analog-to-digital converter, BS beam splitter, CCD CCD camera, MO monitor, PC personal computer.

Theory

Continuum resonance raman scattering in diatomic molecules

The time-dependent and time-independent theory for the calculation of continuum resonance Raman spectra have been described earlier in detail^{4,5,9-11,96-100}. Therefore, we present only a short summary mentioning the important expressions. The standard expression for the Raman scattering intensity, I_{if} , is given by:

$$I_{if} \propto \omega_f^4 N_i g_i |(\alpha_{fi})|^2 \quad (1)$$

where i and f denote the initial and final states of the Raman process, respectively. ω_f is the angular frequency of the scattered light and N_i is the Maxwell-Boltzmann population factor representing the distribution of the initial rovibrational population for an experimentally determined temperature. The intensity dependence on the nuclear spin quantum number is expressed by the nuclear spin factor, g_i .

The Raman scattering tensor, α_{fi} , is traditionally given by the well-known Kramers-Heisenberg-Dirac (KHD) relation:

$$\alpha_{fi} = \sum_{e,n} \frac{\langle f | \mu_{ge} | e, n \rangle \langle e, n | \mu_{eg} | i \rangle}{h(\omega_{e,ni} - \omega_i)} \quad (2)$$

Here, the damping term and the second non-resonant term have been neglected, as described in Ref. 3. $|i\rangle$ and $|f\rangle$ denote the initial and final states of the Raman process, respectively. The continuum states of the excited electronic surfaces, e , are given by $|e, n\rangle$. The dipole matrix elements for the transition between the electronic states g and e are $\mu_{eg} = \mu_{ge}$. In the Condon approximation they are set constant. ($\hbar\omega_i$ is the incident photon energy and $\hbar\omega_{e,ni}$ is the difference between states $|e, n\rangle$ and state $|i\rangle$).

In the equivalent time-dependent theory^{101,102} the scattering tensor α_{fi} depends on the overlap $\langle f | e, \tilde{\tau}(t) \rangle$ of the final state $|f\rangle = \mu_{eg} |f\rangle$ with the initial state $|\tilde{\tau}\rangle = \mu_{eg} |i\rangle$ propagated on the potential energy surface of the electronic excited state, e :

$$\alpha_{fi} = -\frac{i}{\hbar} \sum_e \int_0^\infty \langle f | e, \tilde{\tau}(t) \rangle e^{i(\omega_i + \omega_f)t} dt \quad (3)$$

For the case in which two states of e (B and Π) contribute to the scattering process, the expression for the intensity, I_{if} , is given by:

$$\begin{aligned} I_{if} \propto \omega_f^4 N_i g_i & (M_B^4 R_B |\alpha_{fi}^B|^2 + M_\Pi^4 R_\Pi |\alpha_{fi}^\Pi|^2 + \\ & + 2R_{B+\Pi} M_B^2 M_\Pi^2 [Re(\alpha_{fi}^B) Re(\alpha_{fi}^\Pi) + \\ & + Im(\alpha_{fi}^B) Im(\alpha_{fi}^\Pi)]) \end{aligned} \quad (4)$$

Factors M_B and M_Π represent the electronic matrix elements between the electronic ground state and the excited electronic states B and Π , respectively. The derivation of this equation includes a thorough treatment of the rotational part described by the factors R , as adapted from Ref. 5. Using the theory of irreducible spherical tensors, the factors describing the influence of rotations can be reduced to the simple prefactors R_B , R_Π and $R_{B+\Pi}$ for states B and Π , and for the interference term, respectively. These prefactors depend only on the difference between the final and initial rotational quantum numbers, $\Delta J = J'' - J'$, and the scattering state B and/or Π .

From the vibrational and rotational parameters, the line positions of rovibronic Raman transitions have been calculated by making use of the standard equation for the anharmonic oscillator-rigid rotator model with vibration-rotation interaction:

$$\begin{aligned} \frac{E_{v,J}}{hc} &= \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2 + \omega_e y_e(v + \frac{1}{2})^3 + \\ & \dots + B_e J(J+1) + \dots + \alpha_e(v + \frac{1}{2}) J(J+1) + \dots \end{aligned} \quad (5)$$

where ω_e , $\omega_e x_e$ and $\omega_e y_e$ are the vibrational constants, B_e is the rotational constant, and α_e is the coupling coefficient. Higher order terms can be neglected because the resolution in the experimental spectra, which we simulate in this paper, is only about 1 cm^{-1} . For details about the numerical calculations, we refer to Refs. 9-11, 96, 102.

Franck-Condon theory for one-, two-, and four-photon spectra in polydiacetylene single crystals

In order to perform numerical calculations for the results of absorption, resonance Raman, and resonance CARS spectroscopy, we have developed a theoretical model. This model is based on the KHD formula and includes a variety of special assumptions which are necessary for describing the polymeric system embedded in a crystal matrix. As the complete description of the model is very lengthy here we only list the main assumptions. For a detailed discussion, we refer to Refs. 34 and 35.

As mentioned, the theoretical model is based on the KHD equation. The following points had to be taken into consideration: (i) the system is highly anisotropic: a distribution of conjugation lengths for the delocalized π -electron system of the polymeric backbones, as well as the influence of the surrounding monomeric matrix, is included; (ii) the states are assumed to be Born-Oppenheimer states; (iii) for the electronic wavefunctions, a Herzberg-Teller expansion is applied; (iv) a harmonic oscillator approximation is used together with the assumption that the potentials of ground and excited states are equivalent but shifted; (v) the wavefunctions needed for the calculation of the electronic overlap integrals are derived using a Hückel-MO approximation.

Raman-Mie theory

Linear Raman spectroscopy of bulk samples can be described as inelastic light scattering of the incident photons by the molecules. The frequency-shifted peaks in a Raman spectrum are ascribed to specific molecular vibrations. The intensity of a Raman mode depends on the concentration of a specific molecule, as well as on the Raman cross section of the particular vibrational transition. Since the development of optical levitation⁷¹⁻⁷⁶, various solid^{61,62} and liquid⁶³⁻⁷⁰ microparticles have been studied with Raman spectroscopy using this technique. Raman spectra of such systems were presented by Thurn and Kiefer⁶¹ in 1984. They observed several sharp peaks superimposed on the spontaneous Raman spectra. These peaks are referred to as morphology-dependent resonances (MDRs) or output resonances⁷⁷. The MDRs are standing waves formed by light bouncing around the rim by near-total internal reflection, and correspond to well defined eigenfrequencies with particular resonance radii of the spherical microparticle. When a Raman-shifted frequency coincides with an eigenfrequency (MDR) of the sphere, the Raman cross section is enhanced. The modification to the Raman cross section is related to the Q value of the Raman MDR. In addition, the spatial overlap of the pump laser and the Raman supporting MDR also affects the cross section¹⁰³.

A theoretical description of Raman scattering in spherical microparticles was first given by Chew *et al.* in 1976¹⁰⁴. They describe the problem as statistically distributed dipoles inside the droplet which emit light at the Raman-shifted frequencies. The calculation of the incident, transmitted, as well as the Raman fields inside and outside the droplet, was performed by applying the expansion multipole technique. Theoretical results from these subjects have been published for spheres¹⁰⁵⁻¹⁰⁹, concentric spheres¹¹⁰, cylinders¹⁰⁴, and spheroids¹¹¹.

Results and Discussion

Halogen and interhalogen molecules

The determination of excited state potential functions from resonance Raman spectra

Optimized potential data are obtained by comparing the time-dependent and the time-independent calculations with experimentally observed spectra by means of detailed fitting procedures. As is already known, the intensity of a vibrational transition in continuum resonance Raman scattering strongly depends on the excitation energy. In the case in which more than one excited state contributes to the scattering intensity, the result is not simply the numerical sum of the specific contributions of the single states. According to Eq. 4 there is also destructive or constructive interference between the excited states, depending on the

signs of the real and imaginary parts of the functions α_{fi}^B and α_{fi}^I . To what extent the specific excited states contribute to the continuum resonance Raman scattering intensity is determined by the electronic transition moments, M_e , as well as by the values of the Franck-Condon factors of the vibrational transitions. It should be mentioned in this context that we cannot determine the absolute values of the electronic transition moments, but only the ratio $R = M_B/M_I$. Hence, we took the ratio of the electronic transition moments and the shape and position of the excited states as fit parameters for the simulation of the observed continuum resonance Raman spectra. Thus, theoretical simulations of continuum resonance Raman spectra, with the inclusion of scattering from both states, allow us to derive information about the excited state potential functions with a high degree of accuracy.

In Figs. 3 and 4 we show as examples the experimentally observed (A) continuum resonance Raman spectra of the first overtone ($\Delta v = 2$) of the $^{79}\text{Br}^{35}\text{Cl}$ molecule¹⁶ for one wavelength in the visible and one in the UV region (457.9 and 363.8 nm, respectively), and compare them with numerically calculated spectra by making use of the conventional (KHD) theory (left panel) and the time-dependent theory (right panel). The spectra labeled (B) are the results of calculations where two states, $^3\Pi_{0+}$ and $^1\Pi_1$, have been taken as contributing excited electronic states (all three terms in Eq. 4), whereas in panels C and D the contributions of the single states (only term one and term two of Eq. 4, respectively) are plotted. The theoretical spectra were calculated for the KHD, as well as for the

Figure 3. Continuum resonance Raman spectra of the first overtone transition ($\Delta v = 2$) of $^{79}\text{Br}^{35}\text{Cl}$ with $\lambda_0 = 457.9$ nm excitation. Left panel: (A) experimentally observed spectrum; (B) calculated spectrum applying the conventional (KHD) approach with the inclusion of two excited electronic states ($^3\Pi_{0+}$ and $^1\Pi_1$ state). Spectra C and D represent contributions from the continuum of the $^3\Pi_{0+}$ or $^1\Pi_1$ state alone, respectively. Right panel: spectra B-D are the same as in the left panel, except for the time-dependent theory. The band arising from electronic Raman scattering in the ^{35}Cl atom is marked by an asterisk.

Figure 4. The same as Fig.3, except for $\lambda_0=363.8$ nm.

time-dependent approach. The position and form of the excited state potential functions were varied in order to achieve the best agreement between all measured and calculated spectra.

The calculations show that for 457.9 nm excitation, both potentials contribute to the scattering process (see Fig. 3). The hot band transitions, $Q(3 \leftarrow 1)$, $Q(4 \leftarrow 2)$ and $Q(5 \leftarrow 3)$, originate only from scattering via the $^1\Pi_1$ state (panel D), whereas the fundamental band, $Q(2 \leftarrow 0)$, arises mainly from $^3\Pi_{0+}$ scattering (panel C). The agreement between the calculated (panel B) and experimentally obtained spectra (panel A) is fairly good.

For excitation in the UV region at 363.8 nm (see Fig. 4) the vibrational-rotational structure is quite different from that in the visible region. Here the spectrum is dominated by a strong fundamental $Q(2 \leftarrow 0)$ band, and only a weak first hot band. The calculations reveal that the total spectrum originates from scattering only via the $^1\Pi_1$ state. There is no contribution from the B state, as revealed in the C panels. The Raman intensities in the UV region are mainly dominated by the Franck-Condon factors between the ground and the $^1\Pi_1$ state, and not by the electronic transition moments.

In order to support our interpretation that the $^1\Pi_1$ state plays the exclusive role in the UV region, we measured the depolarization ratios, ρ , of some Raman transitions for different wavelengths in the UV region. Scattering via only the $^3\Pi_{0+}$ state would result in a depolarization ratio of 0.125, and scattering via the $^1\Pi_1$ state results in a value of 0.04 (see Ref. 96). From our experiences, scattering via two states leads to strong wavelength-dependent variations of the depolarization ratios. In Table 2 we have plotted the results obtained for the depolarization ratios, ρ , of the $Q(2 \leftarrow 0)$ transition for three different wavelengths in the UV region. From the values obtained, we can draw the conclusion that the scattering process for excitation in the UV

Table 2. Observed and calculated depolarization ratios of the Q branches for the $Q(2 \leftarrow 0)$ transition ($\Delta v = 2$) of $^{79}\text{Br}^{35}\text{Cl}$ as a function of the excitation laser wavelength.

Excitation wavelength (nm)	Depolarization ratio ρ for the $Q(2 \leftarrow 0)$ band	
	observed	calculated
363.8	0.05 ± 0.015	0.04
351.1	0.06 ± 0.015	0.04
334.5	0.08 ± 0.015	0.04

region exclusively involves a $\Omega = 1$ state. This nicely supports the results derived from the simulations of the observed spectra, as discussed above.

The dependence of continuum resonance Raman spectra on parameters of potential functions

As mentioned above, calculated continuum resonance Raman spectra are very sensitive to the position and shape of the potential functions involved in this type of light scattering. Here we show how the relevant parameters influence the calculated spectra for the $^{127}\text{I}^{79}\text{Br}$ molecule¹⁵, and we compare these spectra to the observed ones. For this demonstration we have chosen the region of the first overtone ($\Delta v = 2$) when excited with seven different laser lines in the visible region ranging from 496.5 to 454.5 nm. We show how the spectral features change when one of the potential functions of the excited states is shifted by a small amount relative to the ground ($^1\Sigma_1$) and excited ($^3\Pi_{0+}$ and $^1\Pi_1$) states. Panel A of Fig. 5 shows the experimentally observed continuum resonance Raman spectra of the first overtone of $^{127}\text{I}^{79}\text{Br}$ excited with seven different laser lines. Panel B represents the corresponding resonance Raman spectra calculated with the KHD theory using the optimized potential functions, while panel C shows the calculated spectra with the $^3\Pi_{0+}$ potential function shifted by 0.01 Å. Although the shift of the potential functions is less than 1 per cent the changes in the spectral features can be clearly recognized, and it may be noted that the experimental spectra are reproduced much better in panel B where the spectra were calculated using the optimized potential parameters.

Symmetry Principle

It has been demonstrated that under certain circumstances, *i.e.* when the intermediate (resonant) Raman levels are the same for Stokes and anti-Stokes Raman scattering, or differ only by a small amount, $\Delta h\omega$ (for details see Refs. 15 and 112), the theoretically calculated spectra for Stokes vs. anti-Stokes are mirror images of each other. This can be shown by applying either the time-dependent or the KHD theory. Figure 6 panel A shows the 454.5 nm excited

Figure 5. (A) Experimentally observed continuum resonance Raman spectra of the first overtone $\Delta v = 2$ of $^{127}\text{I}^{79}\text{Br}$ excited with seven different laser lines, as indicated. (B) Calculated spectra applying time-independent theory with inclusion of both excited electronic states ($^3\Pi_{0+}$ and $^1\Pi_1$), using the optimized potential function data. (C) The same as Panel B, but with the $^3\Pi_{0+}$ potential shifted by 0.01 Å.

spectrum of the first overtone ($\Delta v = 2$) of $^{127}\text{I}^{79}\text{Br}$ together with the simulations as labeled. Panels B and C are anti-Stokes spectra of the same spectral region excited with 465.8 nm and 454.5 nm, respectively. The agreement between the experimental and theoretically calculated spectra is very good for all three cases (panels A-C). However, the spectral feature for the 454.5 nm excited spectrum on the anti-Stokes side is quite different from the one of the Stokes side, whereas the 465.8 nm excited anti-Stokes spectrum is a perfect mirror image, because the difference between the intermediate scattering levels, *i.e.* $\Delta h\nu$, is smaller than 3 cm^{-1} .

Time dependent aspects

The reflection principle. It is well known that in the Condon approximation of the time dependent theory of continuum resonance Raman scattering, the scattering tensor depends on the overlap, $\langle f | \hat{i}(t) \rangle$, of the initial $|i\rangle$ and final $|f\rangle$ vibrational states of the electronic ground state, the former propagated on the potential energy surface of the relevant electronically excited state¹⁰¹. In this connection Kolba *et al.*¹¹³ have shown that the nodal structures of the spatial or momentum representations of $|i\rangle$ or $|f\rangle$ are mapped, in part, on corresponding oscillatory patterns of the fundamental overlap, $\langle f | \hat{i}(t) \rangle$. This reflection principle is, as mentioned by the authors, complementary to previous reflection principles in molecular spectroscopy, where for example, the nodal structures of $|i\rangle$ are mapped on the populations of $|f\rangle$.

As specific examples, we show in Figs. 7 and 8 how the initial state of a Stokes transition in $^{127}\text{I}^{79}\text{Br}$ is mapped on

the time-dependent overlap, $\langle f | \hat{i}(t) \rangle$, as well as on its square of the half Fourier transform of this overlap. The latter corresponds to the excitation profile, and hence to the experimentally obtainable intensity of the Raman band shape. In these figures, the time overlaps and excitation profiles for the overlaps, $\langle f = (v+n) | \hat{i}(t) = v \rangle$ (where $n = 1, 2, 3, 4$ and $v = 1$ (Fig. 7) and $v = 2$ (Fig. 8), respectively) are plotted. These figures represent the scattering process from different initial states, *i.e.* the fundamental transition (Fig. 7) and the first hot band transition (Fig. 8). The A Panels of these figures represent the absolute values of the time-integrated overlaps, $\left| \int_0^t \langle f = (v+n) | \hat{i}(t) = v \rangle dt \right|$,

the B panels the absolute values of the time overlaps $|\langle f = (v+n) | \hat{i}(t) = v \rangle|$, and the C panels the excitation profiles (square of the half Fourier transforms of $|\langle f = (v+n) | \hat{i}(t) = v \rangle|$ as a function of energy), each as a function of time. In these calculations, only the $^3\Pi_{0+}$ state is taken into account because this state is mainly responsible for the continuum resonance Raman scattering in $^{127}\text{I}^{79}\text{Br}$. The B Panels of Figs. 7 and 8 nicely demonstrate how the initial wavefunction ($|i\rangle (=|0\rangle$ in Fig. 7 and $=|1\rangle$ in Fig. 8) is mapped on the time dependent overlaps, $|\langle f = (v+n) | \hat{i}(t) = v \rangle|$, and the same is true for the excitation profiles (the C panels in Figs. 7 and 8). Furthermore, it can be seen that the time dependent overlaps (the B panels of each figure) shift to higher time values with increasing quantum numbers of the final state ($v+n, n = 1, 2, 3, 4$). This effect is a consequence of increasing spatial extensions of

the corresponding wave packets, $|f\rangle$, causing extended periods of overlaps with the propagated initial state, $|i(t)\rangle$. The corresponding excitation profiles (C panels) are broader, with less intensity of the scattered light.

In order to verify these calculations experimental work in the determination of the excitation profiles has been performed in our laboratories¹¹⁴. By means of the deconvolution of high resolution continuum resonance Raman spectra, we were able to derive experimental data and compare them to the excitation profiles of a variety of vibrational transitions (fundamental, hot band and overtone transitions). For a detailed description of the experimental verification of the reflection principle, we refer to Ref. 114. For a comparison of experimental and theoretical excita-

tion profiles, the $^{35}\text{Cl}_2$ molecule is very suitable, since only the repulsive $^1\Pi_u$ state is dominant in the scattering process for excitation with laser lines smaller than about 370 nm, and contributions from the $^3\Pi_{0+u}$ state are negligible in this region. So, the nodal structure of the excitation profiles is not influenced by the contribution of a second excited electronic state, as is the case for other halogen or interhalogen molecules. In Fig. 9, we have plotted the excitation profiles for the $^{35}\text{Cl}_2$ molecule for vibrational transitions starting at $v'' = 0$ in panel A, whereas panel B shows transitions for $v'' = 1$. Experimental scattering intensities could be obtained for five argon ion laser lines in the UV region at 363.8 nm (27488.5 cm^{-1}), 351.1 (28480.9 cm^{-1}),

Figure 6. (A) Experimentally observed continuum resonance Raman Stokes spectrum for the $\Delta v = 2$ transition of $^{127}\text{I}^{79}\text{Br}$, together with a simulation of the spectrum applying the time-dependent and time-independent (KHD) approaches, as indicated. Excitation wavelengths $\lambda_i^S = 454.5$ nm. (B) The same as (A) except for the anti-Stokes spectrum excited with $\lambda_i^{AS} = 465.8$ nm; (C) Is the same as B except for $\lambda_i^{AS} = \lambda_i^S = 454.5$ nm.

Figure 7. The Stokes transition for continuum resonance Raman scattering in $^{127}\text{I}^{79}\text{Br}$ from the initial vibrational state $|i = 0\rangle$ to the final states $\langle f = (0 + n)|$, with $n = 1, 2, 3, 4$ via the electronic state $^3\Pi_{0+}$. (A) Absolute values of the time-integrated overlaps for these transitions, (B) absolute value of the time overlaps $|\langle f = (0 + n)|i(t) = 0\rangle|$, and (C) excitation profile (square of the half Fourier transform of $\langle f = (0 + n)|i(t) = 0\rangle$) as a function of energy, each as a function of time.

334.5 (29897.9 cm^{-1}), 305.5 (32734.9 cm^{-1}), and 300.3 nm (33304.0 cm^{-1}). They are marked by circles and quadrangles for transitions with $\Delta v = 2$ and $\Delta v = 3$, respectively. Note that for better comparison of experimental and theoretical data we have not included the Boltzmann population factor for panel B. Comparing experiment and theory, we found good agreement, particularly for excitation with the laser line at 334.5 nm, which gives the highest Raman intensity for the $v' \leftarrow 0$ transition (panel A), but nearly zero intensity for the $v' \leftarrow 1$ transition (panel B). The other data points also reproduce the theoretically predicted excitation profiles fairly well.

Scattering delay times. In addition to the time-dependent overlaps (Figs. 7 and 8, B panels) and the excitation profiles (Figs. 7 and 8, C panels), the corresponding A panels show the time-integrated values of the complex time-dependent overlaps, $\langle f | i(t) \rangle$, of $^{127}\text{I}^{79}\text{Br}$. In Figs. 7

and 8, panels A the absolute value, $|\int_0^t \langle f | i(t) \rangle|$, is plotted as a function of time. These quantities give evidence of the growth of the overall scattering intensity. These functions do not increase monotonically with time, but show distinct maxima instead. The latter are caused by the oscillatory behavior of the real and imaginary parts of the overlap integrals. The integration over time can lead to smaller intensity values at later times. This effect can be interpreted as a destructive interference of contributions from different time intervals during the propagation of the wave packet. Such calculations are also informative with respect to how long the integration time has to be to get reliable intensity data for the precise simulation of complete continuous resonance Raman spectra. In the A panels of Figs. 7 and 8 we recognize that, depending on the transition involved, at

Figure 8. The same as Fig. 7, except for the transitions starting from $|i=1\rangle$.

Figure 9. Continuum resonance Raman excitation profiles of $^{35}\text{Cl}_2$ for vibrational transitions, as indicated. The full lines represent the time-dependent calculations. Panels A and B represent the profiles for vibrational transitions, which start at $v''=0$ and $v''=1$, respectively. Experimental values are marked by circles for transitions with $\Delta v = 2$ and by quadrangles for those with $\Delta v = 3$.

least some ten fs evolve until the scattering intensity has reached a constant value.

The behavior of the curves displayed in Figs. 7 and 8, panels A, has consequences for the scattering delay times, as defined in Ref. 101:

$$t_{fi} = \frac{\int_0^{t-t_0} dt \left| \frac{d}{dt} \left| \sum_e \int_0^t d\tau \alpha_{efi}(\tau) \right|^2 \right|}{\int_0^{t-t_0} dt \left| \frac{d}{dt} \left| \sum_e \int_0^t d\tau \alpha_{efi}(\tau) \right|^2 \right|} \quad (6)$$

This delay time corresponds to the average propagation time of the wave packet until the molecule returns to its electronic ground state. The definition for the scattering delay time, t_{fi} , and further details are given in Ref. 13 and the references cited therein. In Table 3 we have compiled the numerically calculated values for t_{fi} for various vibrational transitions, $\nu_f \leftarrow \nu_i$, in $^{127}\text{I}^{79}\text{Br}$, including hot bands and overtones. For these calculations, Raman scattering contributions from both electronic states $^3\Pi_{0+}$ and $^1\Pi_1$, were taken into account. Comparing the values for transitions $\nu_f \leftarrow \nu_i$ starting from the same initial state (overtones as given in the rows of Table 3), one notices a general increase in the scattering delay times with an increasing quantum number of final states (ν_f). This effect is also a consequence of increasing spatial extensions of the corresponding wave packets, $|f\rangle$, causing extended periods of overlaps with the propagated initial state, $|i\rangle$.

Calculations of the t_{fi} values for transitions with the same $\Delta\nu$ but higher final states, revealed that there is no strict rule for increasing values. Note, for instance, that the transitions with $\nu_i = 2$ have smaller values than the transitions starting from $\nu_i = 1$. The same holds for the $8 \leftarrow 4$ and $10 \leftarrow 4$ transitions when compared with $7 \leftarrow 3$ and $9 \leftarrow 3$ transitions. The reason for this is the non-monotonic change of the time-integrated overlap, as mentioned above.

Polydiacetylenes

Absorption spectroscopy

The Y zones of partially polymerized DAs are yellow or orange colored. This variation of color is probably caused by changes in the electronic properties of the Y zone. Comparing the absorption spectra of the Y and P zones in the simplest case, we find spectra like those shown in Fig. 10a (TS/FBS DA crystal). For the Y zone absorption spectrum, one additional blue shifted band can be found which is accompanied by a P absorption band. The Y absorption shows a similar vibronic structure when compared to the absorption spectrum of the polymer chains³³. Consequently, it is reasonable to assume that polymer chains cause the Y absorption, which is in agreement with the statements made in the introduction. In the P zones, all polymer chains are parallel in orientation. Therefore, the absorption in the visible spectral range (due to the delocalized π electrons) is strongly polarized (dichroism). As the absorption of the Y zones is also polarized parallel to the crystal b axis it can be concluded that the polymer structures responsible for the Y absorption are also oriented parallel to the b axis.

However, in most cases the Y zone absorption is much more complicated. Fig. 10b shows typical absorption spectra for the Y zones of FBS DA crystals. The Y absorption differs substantially from the one reproduced in panel a. The 0-0 line belonging to the P absorption is at about 17000 cm^{-1} . From the position of the absorption peak, it can be concluded that the polymer chains have a length of less than 20 monomer units¹¹⁵. There are several broad bands belonging to the additional Y absorption. The variation of the color of the Y zones seen in different DA crystals can also be observed in the absorption spectra. In both Y absorption spectra the vibronic structure of the bands is not resolved, and therefore absorption spectroscopy alone, even if performed at low temperatures, does not give sufficient information.

Resonance Raman scattering

A good way to derive additional information about electronic as well as structural properties is through reso-

Table 3. Scattering delay times for continuum resonance Raman scattering of $^{127}\text{I}^{79}\text{Br}$ ($\lambda_{\text{exc.}} = 488.0 \text{ nm}$) for several vibrational transitions, $\nu_f \leftarrow \nu_i$.

Transition $\nu_f \leftarrow \nu_i$	Scattering delay time τ/fs	Transition $\nu_f \leftarrow \nu_i$	Scattering delay time τ/fs	Transition $\nu_f \leftarrow \nu_i$	Scattering delay time τ/fs	Transition $\nu_f \leftarrow \nu_i$	Scattering delay time τ/fs
$1 \leftarrow 0$	6.4	$2 \leftarrow 0$	8.4	$4 \leftarrow 0$	12.9	$6 \leftarrow 0$	17.5
$2 \leftarrow 1$	8.6	$3 \leftarrow 1$	11.1	$5 \leftarrow 1$	15.2	$7 \leftarrow 1$	18.5
$3 \leftarrow 2$	6.4	$4 \leftarrow 2$	8.3	$6 \leftarrow 2$	11.2	$8 \leftarrow 2$	14.3
$4 \leftarrow 3$	12.5	$5 \leftarrow 3$	13.8	$7 \leftarrow 3$	16.4	$9 \leftarrow 3$	17.7
$5 \leftarrow 4$	13.2	$6 \leftarrow 4$	14.1	$8 \leftarrow 4$	15.4	$10 \leftarrow 4$	17.2

Figure 10. Absorption spectra of DA crystals having color zones recorded at a sample temperature of 10 K. The polarization of the transmitted light is parallel to the crystal *b* axis. (a) Absorption spectra of the Y and P zones of a TS/FBS DA crystal. (b) Absorption spectra of the Y zones of two FBS DA crystals.

nance Raman spectroscopy. Many investigations concerning chromatic properties^{32,116-119} were made on PDAs by Raman spectroscopic methods. In none of these have problems been reported when taking Raman spectra from different color forms of the PDAs. We noticed that in FBS crystals, luminescence can be observed when the Y zone is irradiated by light with energy higher than the Y absorption. This luminescence is structured and is extremely strong. Because of this luminescence, resonance Raman spectroscopy with excitations suitable for an investigation of the color zones is not possible.

There are several possibilities for obtaining information on Y zones from resonance Raman spectra. One is to investigate Y zones of crystals with very weak color zones by varying the excitation frequency and resonantly enhancing the different electronic transitions. By this method the intense background arising from the luminescence of the Y zone has to be dealt with. Another method is to excite the Raman spectra of crystals with very strong color zones out of resonance, *i.e.* a low frequency excitation, and comparing the spectra of the P and Y zones. In this case, the Raman spectrum is a mixture of contributions from all electronic transitions. Neither of these methods is really satisfactory.

PDA chains, if resonantly enhanced, exhibit only a few Raman lines, all of which belong to symmetric A_g modes of the PDA backbone¹²⁰. In the wavenumber region from 3500 cm^{-1} to 500 cm^{-1} , only four prominent Raman lines, labeled ν_1 to ν_4 , and about six combination frequencies can be seen if resonance conditions are fulfilled¹²¹. Fig. 11 shows a part of the resonance Raman spectrum of the P zone of an FBS DA crystal. The ν_1 line at about 2040 cm^{-1} belongs to the polymer chains in the P zone (later called ν_{1P}), and can be assigned to the $\text{C}\equiv\text{C}$ stretching mode. The

Figure 11. A resonance Raman spectrum of a TS/FBS DA crystal recorded at 10K. The polarization of the exciting laser as well as the detection are parallel to the crystal *b* axis.

doublet at about 1470 cm^{-1} and 1455 cm^{-1} is the ν_2 mode ($\text{C}=\text{C}$ stretching, later called ν_{2P} for the P chains), which is coupled by a Fermi resonance to the CH_2 scissor vibration (ν_{CH_2}) belonging to the sidegroup¹²².

Coherent anti-Stokes Raman scattering

The DA crystals are extremely sensitive to heating, which leads to a further polymerization or to a destruction of the DA crystal. Therefore, laser irradiation with frequencies in resonance with the strong absorption of the polymer chains changes spectral conditions or even destroys the crystal. Even cooling the crystal to about 10 K does not prevent destruction of the crystal if moderate laser power is employed. With the application of very little laser power, constant conditions in the crystals could be achieved when irradiating the sample. Anti-Stokes Raman spectra would

be free of luminescence. However, since the crystal has to be cooled to about 10 K, there is no longer observable Raman intensity for the modes to be detected. However, CARS spectroscopy seems to be a favorable method for obtaining information on both electronic and structural properties. Recent CARS investigations⁹⁴ showed that it is possible to obtain coherent anti-Stokes Raman signals with a fairly good signal to noise ratio. For a detailed description of the CARS process, refer to Refs. 123 and 124.

Before we can make use of the CARS data of the Y zones, it is necessary to have further information at hand concerning the vibrational spectra of PDA chains. Therefore, a careful investigation of the polymers in the P zone by means of resonance Raman spectroscopy was performed first. It has to be kept in mind that the optical spectra obtained from DA crystals are not homogeneous in origin. There is a distribution of conjugation lengths, and also inhomogeneous broadening due to the varying surroundings of the polymer chains. A change in the Raman excitation frequency results in a change in the resonance conditions. This can be seen not only from the changing Raman line intensities but also from the change in their shapes.

Fig. 12 shows some examples of resonance Raman excitation measurements. The panels on the left display excitation profiles for the ν_{1P} and ν_{2P} modes of an FBS

DA crystal, as well as its absorption spectrum. The dots are the experimentally obtained line intensities, while the full lines are simulations. Raman line profiles obtained for different Raman excitation wavelengths (labeled in each panel) are presented on the right side of Fig. 12, together with simulations. The calculated excitation profiles and line shapes were obtained using the theoretical model³⁵ mentioned earlier. These simulations enable us to describe both the electronic and vibrational properties of the PDA chains. The results from the investigation of the P zones can now be used to interpret the results obtained by CARS spectroscopy on the Y zones of different DA crystals.

Varying the pump laser frequency, ν_{pu} , enables the investigation of the resonance behavior of the CARS lines. Such CARS excitation spectroscopy yields results comparable to those obtained from linear Raman spectroscopy. From the CARS experiments on P-form DA crystals, we expect an extreme enhancement of the signal when in resonance with the ${}^1A_g - {}^1B_u$ transitions of the delocalized π electron system of the polymer backbone. The nonlinear optical properties of PDAs showing chromisms have already been investigated³³. It was shown by third harmonic generation measurements that the Y form of the investigated PDA films also exhibits remarkable values for the third-order non linear susceptibility ($|\chi^{(3)}|$) which are only a little smaller than those measured in P-form films.

Figure 12. Excitation profiles (left panels) and resonance Raman spectra (right panels) of the P zone of an FBS DA crystal recorded at 10 K. The lower curves are the measured Raman line shapes and the upper curves show the results of simulations.

Figure 13 shows CARS spectra obtained from an FBS DA crystal in the Y zone. The spectra were taken for different pump laser wavelengths, λ_{pu} , as labeled in the panels. The spectra presented are all corrected for different laser intensities, detection sensitivity, and linearity, and also for absorption. The scales for the CARS intensities are therefore comparable to each other. For comparison, we also show the absorption spectrum where the pump excitation is marked.

Before discussing the CARS spectra we would like to emphasize two crucial points which have to be considered when CARS spectra are taken from these crystals. As mentioned above, the crystals are very sensitive to laser light, which forces the use of very low laser power. Especially in the Y zone, we observe changes in the CARS spectra if too high a laser power is employed. The spectra obtained at very low laser power (of the order of 1 to 10 μ J) were repeated several times. Even under these conditions, we sometimes were unsuccessful in recording CARS spectra when excited at an exact resonance within the electronic 0-0 transition. The noise inherent in the unsmoothed CARS spectra therefore originates from the low laser power employed.

The second point worth mentioning is that both the intensity and frequency of the CARS lines (the same is valid for Raman) may shift considerably when changing

Figure 13. Resonance CARS spectra of an FBS DA crystal recorded at 10 K. For comparison, the absorption spectrum is added where the position of the pump excitation is marked.

the spot position on the crystal surface. This arises from inhomogeneities in the monomer crystals, and reveals a distribution of relatively short chains in their monomer matrices. As previously shown^{35,125}, short chains (up to about 30 monomer units) have discernible optical properties. Comparisons are therefore only meaningful if complete spectra are taken from one crystal spot in the actual color zone, containing the ν_{1P} , ν_{2P}/ν_{CH2} , and ν_{1Y} , ν_{2Y} modes. Changing the laser dyes is therefore not possible while taking the spectrum, which would otherwise require a realignment of the laser beams. Only if ν_{pu} had to be changed, were different dyes used. In this case we always tried to hit the same spot in the crystal. There are relatively few combinations of dyes for pump and Stokes lasers which allow taking CARS spectra over a complete range of about 900 cm^{-1} . As a consequence, we could only choose a specific set of values for ν_{pu} .

The phase matching conditions were kept as follows. The phonon momentum vector, $\vec{k}_{phon}$, was set parallel to the b axis, which means parallel to the extent of the conjugated π electron system of the polymer backbones. For other cases, no remarkable CARS signal could be detected. The applied phase angle, Θ , was relatively small (1° - 3°) and had no measurable dispersion. In addition, there was no difference in the Θ for the P and Y zones. This fact can be easily explained. The DA crystals represent a system which can be compared with a solution at a low concentration, where the polymer chains are randomly distributed in the monomer matrix. Therefore, the phase angle is determined by the monomers, rather than by the polymers, as long as the concentration is not too high. The monomer matrices do not absorb in the visible range and therefore the refractive index does not show remarkable dispersion in this region. This results in a small, nearly constant phase angle. The polarizations of the ν_{pu} , ν_{St} , and ν_{as} beams were chosen to be parallel to the chains.

The CARS spectra in Fig. 13, together with the absorption spectra allow insight into the nature of the Y zone. As an example, we show CARS spectra around the ν_2 mode of the polymer backbone. The spectra of the P zone only exhibit the ν_{1P} and ν_{2P}/ν_{CH2} lines for all pump laser wavelengths, λ_p . The same lines can be observed in the Y zone when exciting near the $P-(^1A_g-^1B_u)$ transition. For this case, almost no additional features in the spectrum are found, as can be seen in Fig. 13 for $\lambda_{pu} = 598$ nm. Here, only a slight indication for a new line can be seen at higher wavenumbers. At about this position a new band occurs for 557 nm excitation. This band seems to have contributions from at least two lines. ν_{2P}/ν_{CH2} can still be clearly recognized.

The pump laser wavelength at 557 nm is located on the Stokes wing of a band which shows up strongly in the absorption spectrum of the Y zone at about 18400 cm^{-1} .

Note that the band at about 18300 cm^{-1} in the absorption spectrum of the P zone is of a vibronic nature. The next λ_{pu} at 532 nm is on the anti-Stokes side of this feature. ν_{2Y} is positioned in the lower energy region of the broad band displayed for $\lambda_{pu} = 557\text{ nm}$. This indicates that two lines are hidden there. These bands are assigned to polymer chains with two different $^1A_g \rightarrow ^1B_u$ transitions. With 532 nm excitation mainly the higher energy transition is in resonance, which results in an enhancement of the associated ν_{2Y} line.

To investigate the next strong band at about $20,700\text{ cm}^{-1}$ in the Y absorption spectrum, we chose wavelengths at 510 nm and 488 nm for the pump laser beam. For both excitations, new ν_{1Y} and ν_{2Y} lines show up in the same spectral position, which is shown in Fig. 13 for the ν_2 mode. This band is shifted to lower wavenumbers, as compared to the band observed for 532 nm . For λ_p at 488 nm , we placed the excitation wavelength near the maximum of the strongest feature of the Y absorption spectrum. Because of very high absorption for this wavelength we succeeded in taking CARS spectra without destroying the crystal at the spot where the focus of the pump and Stokes lasers hit the crystal surface only after several attempts. The observed ν_{2Y} and ν_{1Y} lines are very strong. This is indicated by an arrow in Fig. 13 for the ν_{2Y} line. These bands also have about the same width and position as the CARS lines observed for 510 nm excitation. No enhancement of any other CARS lines can be seen when varying the pump laser wavelength from 510 nm to 488 nm . This indicates that no more $^1A_g \rightarrow ^1B_u$ 0-0 transitions are made between the two strong absorption bands belonging to the Y zone. The experimental limit for λ_p was at about 460 nm . However, in the region $488\text{ nm} > \lambda_p > 460\text{ nm}$ we were unable to obtain reliable CARS spectra because of a fast decrease of line intensity, most probably originating from the destruction of the sample. The observed line positions remained at about the same wavenumber region as those observed for 488 nm excitation.

A model for the chromism effect

We believe that our measurements strongly support the model which explains the chromism effect by a change in the conjugation length of the π electron system of the polymer backbone. By applying resonance Raman and resonance CARS spectroscopy, selective enhancement of vibrations is possible for those domains where electronic transitions coincide with the excitation wavelength. The FBS DA crystals studied in our investigations revealed at least five new domains in the Y zone in addition to the P domain.

Further proof for our hypothesis may be given by comparing the 0-0 transition energies of short P oligomers³³

with those resonance energies found from CARS excitation spectroscopy. This is shown in Fig. 14 for FBS DA crystals. The transition energies of the P oligomers as a function of the conjugation length can be described well using a Hückel molecular-orbital model. We find that the resonance energies seen in the Y zones can also be described by this method if only an energy shift of about 1000 cm^{-1} is assumed. It is very interesting that for the Y zone only conjugation lengths with even numbers of monomer units can be found.

The question remains as to whether shorter chain lengths or interruptions of longer chains are responsible for the occurrence of chromism in DA crystals. Both effects would explain a blue shift in absorption, as has been shown by Exarhos *et al.*³² who applied a simple free electron gas model to PDAs. There are two points which support the assumption that the interruption of the conjugation is the reason for the observed features seen in the DA Y zones. First, there is no conformity between the observed features found in Y absorption spectra with measured absorption of DA oligomers^{33,115}. Second, if there were separate short chains, one would expect a blue shift in absorption for decreasing chain length combined with an increase of the Raman frequency for the C=C and C≡C stretching modes. Such observations have been made for t-butyl capped polyenes¹²⁶ and for polyacetylenes¹²⁷. However, our results are contrary to these observations. The measured positions for the CARS lines shift to lower energies when excitation is coming into resonance with the electronic transition of higher energy.

Investigations of PDA and DA crystals containing defects showed that luminescence occurred near defects if irradiated by blue light^{33,128}, similar to that observed for Y zones. Fluorescence spectroscopy of stable DA oligomers also exhibits structured spectra, while defect-free PDA crystals containing long polymer chains do not show remarkable luminescence¹²⁹. Defects as the proper cause of chromism in the three mentioned DAs, FBS, TS6, and

Figure 14. Energies of 0-0 transitions in FBS DA crystals with color zones.

TS/FBS, may be confirmed by the following experimental results.

The observation of sharp color zones in DA crystals was first described for TS/FBS crystals³³. TS6 crystals sometimes showed color zones, whereas in FBS crystals these color zones were more frequently observed. The appearance of color zones seems to depend on the growth condition of the crystals. On the {100} surface of the crystals zones of different roughness could be observed. These surface zones, in most cases, correspond to the P and Y zones of the crystals. This observation makes it most probable that crystal defects interrupt the conjugation of the p electron system, which leads to shorter conjugation lengths as a consequence of higher absorption frequencies. Recently, Eckardt *et al.* suggested that the high energy shift in absorption as well as in the stretching frequency originating from a P to Y form change in PDAs, can be understood as an effect of strain induced by substituents³¹. These authors used VEH and MNDO calculations to explain the influence of the side group angle relative to the PDA backbone on the optical properties of PDAs. They found that side group distortions needed to produce spectral shifts seen for chromatic transitions only lead to subtle rearrangements of backbone geometry. Crystal defects, which are only a small hindrance for the side groups could therefore effect the formation of Y zones. The different frequency of the appearance of color zones in DAs containing different substituents (see Table 1) strongly points to a primary role of side group geometry as the cause for chromism.

There are still two essential questions open: (i) why do the observed CARS frequencies of the Y chains shift to lower values for shorter conjugation lengths? As discussed above, an opposite effect is expected. A possible explanation for this is that the defects locally influence the Y chains. These defects try to turn the side groups, which results in a blue shift for the absorption as well as for the Raman frequencies. If only one substituent is turned in relation to the others, the strain should be larger than for the case in which more substituents are turned in the same direction. Therefore, a separation into shorter parts results in a more relaxed chain with a Stokes shift for the vibrational frequencies. However, we must mention that no experimental proof can be given for this explanation when applying the methods discussed above. A calculation similar to the one reported by Eckhardt *et al.*³¹ would definitely give more insight into this problem. (ii) The second question is why there exist sharply separated color zones rather than a homogeneous distribution of Y chains over the whole crystal. Different investigations (see Ref. 33 and references therein) have shown that edge dislocations are preferably situated in {111} growth sectors. A strain field on monomer molecules is forced by small-angle grain boundaries formed by dislocations having a Burgers vector in the *b* direction ([010]). Taking into account the argu-

ments given above, the origin of color zones in DA crystals may be explained by supposing that the {111} growth sectors coincide with the observed color zones. This would also explain why an interruption of the conjugation occurs only in distances of two monomer units, as each crystal unit cell contains two monomer units.

Finally, accepting this model we can combine the parameters obtained from the simulations of the spectra of the P and Y zones. We used the model to calculate the absorption spectra of the different Y zones. Details of these calculations are given in Ref. 35. In Fig. 15 the results are shown for the two spectra presented in panel b of Fig. 10. Only one parameter, the absolute optical density, was varied for the simulations. The calculated spectra resemble the experimental absorption spectra very closely.

Morphology-dependent resonances in microdroplets

Radius and refractive index determination

The experimental setup described above allows the levitation of numerous kinds of liquid droplets, and thus their investigation by use of Raman-Mie scattering^{78,84-87}. Three typical Raman spectra in the region of the OH-vibration (3100-3500 cm⁻¹) of an optically levitated glycerol droplet are presented in Fig. 16. Within the recorded spectral range, 13 sharp peaks (labeled 0 to 12 in Fig. 16), which can be identified as output MDRs, are superimposed on the broad Raman signal. The spectra shown in Fig. 16A-C were observed at 149 s, 172 s, and 180 s, respectively, after

Figure 15. Y zone absorption spectra of FBS DA crystals (compare with Fig. 10b) and their simulations.

Figure 16. Raman spectra in the region of the OH-vibration ($3100\text{--}3500\text{ cm}^{-1}$) of an optically levitated glycerol droplet; 13 output morphology-dependent resonances (MDRs) (labeled 0 to 12) are superimposed on the broad Raman signal. The spectra A-C were observed at 149 s, 172 s, and 180 s, respectively, after starting the measurement. The integration time for the spectra is 0.9 s.

starting the measurement. Spectra were taken every second, with an integration time of 0.9 s. A short integration time is necessary to temporally resolve the spectral location of output MDRs. Therefore, the signal-noise ratio is not very high. Nevertheless, output MDRs of a microdroplet are easily distinguished from the noise. Each output MDR is sufficiently defined by a particular resonance Mie-size parameter, $x_{\text{res}}(m)$ ($x = 2\pi a/\lambda$, where a is the droplet radius and λ is the MDR wavelength), which is constant if the corresponding relative refractive index, m ($m = m(\text{inside})/m(\text{outside})$), does not change^{80,82,106}. When a droplet evaporates, its radius, a , continuously decreases, which causes a decrease of the wavelength, λ , of the output MDRs in the Raman spectra. The vertical lines in Fig. 16A-C illustrate the time dependence of the output MDR movement to smaller wavenumber shifts. Therefore, the peaks labeled with an x do not correspond to output MDRs.

The droplet evaporation was also investigated by MDR movement in Raman spectra by displaying the Raman shifts as a function of time in a two- or three-dimensional plot. Fig. 17B shows a three-dimensional plot of the time-

Figure 17. (A) A contour plot of Raman-spectra of the CH-vibration region ($2800\text{--}3000\text{ cm}^{-1}$) of evaporating glycerol droplet versus time. (B) The same as in A, but as a three-dimensional plot.

resolved Raman spectra of an evaporating glycerol droplet investigated in the CH-vibration region ($2800\text{--}3000\text{ cm}^{-1}$) over a time range of 0 to 400 s. The observed output MDRs move towards smaller relative wavenumbers, which indicates that the droplet radius is decreasing. When a droplet eigenfrequency coincides with the incident laser frequency the whole Raman spectrum is enhanced. In these cases, the resonant coupling increases the internal electric field intensity, and hence, the total Raman intensity⁷⁷. These input MDRs can be identified by looking at the three-dimensional plot from the top, which is shown in Fig. 17A. A contour plot of the Raman intensities as a function of time is presented here. With both display methods it is possible to easily distinguish between narrow vibrational Raman peaks, input MDRs and output MDRs.

Input and output MDRs are classified by a_n , b_n and c_n , d_n coefficients^{70,82,87,106,130-132},

$$a_n = \frac{\psi_n(x) \psi'_n(mx) - m \psi_n(mx) \psi'_n(x)}{\zeta_n(x) \psi'_n(mx) - m \psi_n(mx) \zeta'_n(x)}$$

$$b_n = \frac{m \psi_n(x) \psi'_n(mx) - \psi_n(mx) \psi'_n(x)}{m \zeta_n(x) \psi'_n(mx) - \psi_n(mx) \zeta'_n(x)} \quad (7)$$

$$c_n = \frac{-im}{\zeta_n(x) \psi'_n(mx) - m \psi_n(mx) \zeta'_n(x)}$$

$$d_n = \frac{-im}{m \zeta_n(x) \psi'_n(mx) - \psi_n(mx) \zeta'_n(x)} \quad (8)$$

where the a 's and the c 's are the TM (transversal magnetic) and the b 's and the d 's are the TE (transversal electric) modes of the external and the internal fields, respectively. The resonance locations are found by setting the denominators to zero. The result for each mode number n yields multiple resonances corresponding to radial mode order l , and is denoted as $x_{n,l}$. The subscripts n and l describe the number of intensity peaks along a half circle and the radius of the droplet, respectively. ζ and ϕ are the well-known Ricatti-Bessel functions. All modes are associated with a particular resonance Mie-size parameter, $x(m)_{n,l}$, and a particular relative refractive index, m .

Therefore, assignment of experimentally observed MDRs in optical spectra to theoretically determined modes allows a precise determination of the droplet size a , refractive index m , and the wavelength dependence of the refractive index D , of a single microparticle^{78,79}. A new algorithm has been developed for this purpose. The main feature of the new algorithm is that the Mie calculation of the MDR location is separated from the algorithm which assigns MDRs and determines droplet properties¹³³. This separation results in improved computation time.

The accuracy of the results of the output MDR evaluation algorithm is verified by simulating the measured Raman spectra^{83,108}. The calculations are based on the method developed by Chew *et al.*¹⁰⁴. In Fig. 18 the experimental (panel A) and the simulated (panel B) Raman spectra of an optically levitated tetraethylene droplet are shown¹³⁴. The experimental spectra are taken in the CH-vibrational region (2700–3100 cm⁻¹) at $t = 10$ s, 20 s, 30 s, and 40 s after starting the measurement. The observed output MDRs are identified as d_{72}^3 , d_{68}^4 , and d_{73}^3 modes. The calculated spectra are in good agreement with the experimentally observed Raman spectra. Furthermore, the movement of the output MDRs, attributed to droplet evaporation, is also reproduced well. The time dependence of the radius and the refractive index were determined to be:

$$m(t) = 1.45602 - 1.760 \times 10^{-7} \text{ s}^{-1} \cdot t \quad (9)$$

$$a(t) = 6.005 \text{ } \mu\text{m} - 4.40 \cdot 10^{-4} \text{ } \mu\text{m s}^{-1} \cdot t - 2.182 \times 10^{-10} \text{ } \mu\text{m s}^{-2} \cdot t^2 \quad (10)$$

The laser power, as well as the Mie scattering intensity, are recorded simultaneously with the Raman spectra. The laser power is proportional to the radiation pressure exerted on the microdroplet and inversely proportional to the radiation pressure efficiency, Q_{pr} . Therefore, the time dependence of the radius $a(t)$ and refractive index $m(t)$ may be

Figure 18. The comparison of observed (A) and calculated (B) Raman spectra of an evaporating tetraethyleneglycol droplet; CH-vibrational region (2700–3100 cm⁻¹) at $t = 10$ s, 20 s, 30 s, and 40 s after starting the measurement.

checked by calculating both the elastically scattered light intensity¹³³ and the inverse of the radiation pressure efficiency ($1/Q_{pr}$)^{78,85,86}. The expression for the time-dependent radiation pressure is:

$$Q_{pr}(m(t), a(t)) = Q_{pr}(m_0 + m_1 \cdot t + m_2 \cdot t^2 \dots, a_0 + a_1 \cdot t + a_2 \cdot t^2 \dots) \quad (11)$$

where the m_i and a_i are polynomial coefficients, which describe the time dependence of the radius and the refractive index, respectively, and Q_{pr} is defined as^{80,82,106,135}:

$$Q_{pr} = Q_{ext} - \frac{4}{x^2} \sum_{n=1}^{\infty} \frac{n(n+2)}{n+2} \text{Re}(a_n^* a_{n+1} + b_n^* b_{n+1}) + \frac{2n+1}{n(n+1)} \text{Re}(a_n^* b_n) \quad (12)$$

$$Q_{ext} = \frac{2}{x^2} \sum_{n=0}^{\infty} (2n+1) \operatorname{Re}(a_n + b_n) \quad (13)$$

Q_{ext} is the extinction efficiency factor. These calculations also reveal the accuracy of the evaluated wavelength dependence, D , of the refractive index by analyzing the output MDRs in Raman spectra¹³³. The actual refractive index for the laser wavelength is found by use of the following dispersion relation:

$$m = n + D(\nu_0 - \nu) \quad (14)$$

where ν is the absolute wavenumber in the center of the Raman spectrum, ν_0 is the wavenumber of the laserline, n is the evaluated refractive index at ν , and D is the dispersion value. The results of such a calculation (shown in Fig. 19B) are compared with the experimentally monitored laser power (shown in Fig. 19A). The sharp dips in both sets of data are caused by input MDRs⁸⁶ (labeled 0 to 16 in Fig. 19A). Assigning the experimentally observed input MDRs to theoretically calculated modes of the external field reveals that the input MDRs can be divided into groups of MDRs with the same radial order l and decreasing mode number n . For example, the MDRs 0, 3, 7, 10, 13, and 16 are connected to a_n modes with $l = 6$, and the MDRs 2, 5, 8, 11, and 14 correspond to a_n modes with $l = 5$. The MDRs labeled with an x in Fig. 19B are not observable in the experimental data because the time resolution of the calculation is better than that of the experiment. The agreement between the calculated and measured data is fairly good.

Temperature behavior of an evaporating droplet

The determined time dependence of the radius ($a_0 + a_1 t + a_2 t^2 \dots$) and refractive index ($m_0 + m_1 t + m_2 t^2 \dots$) has been used to study the temperature behaviour of an evaporating microdroplet^{79,88}. It has been experimentally observed that the spectral location of output MDRs suddenly changes when a droplet eigenfrequency coincides with the laser frequency. Each time the droplet radius corresponds to that of an input MDR, the amount of energy that is transferred from the external light field into the sphere increases. Even though the droplet absorbs weakly, heating becomes significant when the large resonant internal field intensity is dissipated within the droplet. As a result of increased droplet temperature, output MDRs in the Raman spectra suddenly move towards smaller wavenumber shifts. Fig. 20 shows the experimentally observed laser power in panel A and the calculated inverse radiation pressure, $1/Q_{pr}$, in panel B. Using the temporally resolved radius and refractive index of the droplet we are able to calculate the droplet absorption efficiency factor, Q_{abs} , which is defined as:

$$Q_{abs} = Q_{ext} - Q_{sca} \quad (15)$$

where Q_{sca} is the scattering efficiency factor

Figure 19. (A) The time dependence of laser power to optically levitate a triethyleneglycol droplet; (B) theoretically calculated inverse radiation pressure efficiency, $1/Q_{pr}$.

Figure 20. (A) Time dependence of laser power to optically levitate a triethyleneglycol droplet; (B) theoretically calculated inverse radiation pressure efficiency, $1/Q_{pr}$; (C) output morphology-dependent resonances (MDRs) located in Raman spectra; (D) calculated change of temperature; (E) calculated absorption efficiency factor. The observed input MDRs in panel (E) are assigned to the modes of the external field.

$$Q_{sca} = \frac{2}{x^2} \sum_{n=0}^{\infty} (2n+1) [|a_n|^2 + |b_n|^2] \quad (16)$$

The calculated results of Q_{abs} are presented in panel E of Fig. 20. The observed input MDRs are assigned to the a_n and b_n coefficients of the external field. In panel C the locations of the output MDRs are displayed as a function of time. The smooth linear shift of the MDRs is interrupted by small spectral jumps corresponding to strong input MDRs^{70,136}. Vertical lines are drawn in Fig. 20 to emphasize this behavior.

The spectral shifts of the output MDRs can be understood by considering the refractive index dependence of the resonance Mie-size parameter $x_{n,l}$. An input resonance increases the temperature of the droplet, decreasing the refractive index, thus increasing $x_{n,l}$. This increase in $x_{n,l}$ moves the MDR locations towards smaller wavenumber shifts. The change of droplet temperature can be calculated (see Fig. 20D) based on a steady state energy balance between the absorbed laser light and the thermal heat loss. The effect of evaporative cooling is ignored because the temperature of the surrounding atmosphere in our experiments is always higher than the droplet surface temperature. Fig. 20C also indicates that as the laser light becomes non-resonant due to evaporation, the droplet returns to its original temperature and the output MDR wavenumber resumes its linear progression.

Applications

The results presented illustrate that MDRs observed in optical processes can reveal the physical properties of droplets. Therefore, the application of optical levitation in combination with Raman-Mie-scattering and radiation pressure measurements to environmental as well as industrial problems is practical.

Microchemical reaction studies at the gas-liquid surface are important in the investigation of tropospheric cloud chemistry and many industrial processes. Using the analytical methods discussed, we are able to quantitatively describe a controlled acid/base reaction between a capric-acid/heptanol droplet and gaseous ammonia^{57,137}. This reaction between an optically levitated acid droplet and a reactive gas results in the formation of a solid salt layer. The thickness and the homogeneity of a salt coating formed depends on the evaporation rate of the acid droplet as well as on the concentration of the reactive gas in the surrounding medium. The formation of the salt layer has been proven by two independent measurements: (1) the time dependent movement of the output MDRs in the Raman spectra of the microdroplet and (2) the Raman spectra in the vibration region of solid salt. Fig. 21B shows one particular output MDR observed in the CH-stretching vibration region (2800–3000 cm^{-1}) of a capric-acid/heptanol

Figure 21. (A) A model of the evolution of the acid/base reaction: on the left side the evaporation of the droplet is shown, in the middle gaseous ammonium diffuses to the surface of the acid droplet, and on the right side the coated microdroplet is shown. (B) Movement of a particular output morphology-dependent resonance (MDR) in the time interval $t = 190$ to 230 s.

droplet as a function of time. In the time interval from 190 to 200 s the observed MDR moves towards smaller wavenumber shifts, caused by droplet evaporation. At $t = 200$ s, NH_3 insertion into the chamber starts. The MDR immediately begins to change its location towards larger wavenumber shifts. After 10 s the MDR movement stops.

A model of the evolution of the reaction is shown in Fig. 21A. In the first part of the picture the evaporation of the microdroplet is presented. After starting the NH_3 insertion into the chamber, gaseous ammonia diffuses towards the acid droplet (second part of Fig. 21A). The base reacts at the surface of the acid microdroplet and a solid layer of salt builds (third part of Fig. 21A). This shell, built up on the droplet surface, forms a barrier between the gaseous ammonia and the acid droplet, stopping the reaction. There is at most no further evaporation of the microdroplet. This can be seen in the nearly constant position of the output MDR. The spectral change of the MDR location of about 125 cm^{-1} towards larger wavenumber shifts is connected to the formation of a $\approx 45 \text{ nm}$ ammonium salt layer. The ammonium salt formation is verified by taking Raman spectra in the wavenumber region of $75\text{--}150 \text{ cm}^{-1}$ and comparing those droplet spectra with spectra from bulk investigations. The droplet Raman spectra before the reaction and after the reaction are presented in Fig. 21C and D, respectively. After the reaction, the vibration of the ammonium salt formed can be observed. Further investigations with other acids and bases as well as with various concentrations of reactive gases have been conducted⁵³. We found that these reactions always result in the formation of a solid salt layer. In the case of low gas concentration, the shell was not thick enough to prevent droplet evaporation. The incomplete

coating results in a decrease of the droplet evaporation rate, which can be seen in the change of the input MDR pattern of the incident laser power vs. time. The time interval between input MDRs increases if the evaporation rate decreases⁵³.

Polymerization and copolymerization reactions relevant for industrial applications have also been studied. The first Raman investigation of the emulsion polymerization of styrene to polystyrene in a single emulsion particle was performed by Urlaub *et al.*¹³⁸. Recently, the radical polymerization and copolymerization reaction was investigated in styrene and unsaturated polyester-resin (UP-resin) microparticles by Musick *et al.*⁸⁹.

A condensation reaction of maleic acid and glycol forms the UP-resin under investigation. The reaction was started using a dibenzoylperoxide radical-initiator. The reaction was observed temporally by investigating the chemical composition using Raman spectroscopy. Raman spectra taken in the region between 1550 and 1800 cm^{-1} as a function of time are displayed in Fig. 22. The phenyl-vibration and the double bond vibration of styrene are recorded at 1596 cm^{-1} and 1628 cm^{-1} , respectively. The latter decreases in a short time and describes the polymerization. The maleic acid C=C double bond mode and the C-O stretching of UP-resin are observed at 1655 cm^{-1} and 1725 cm^{-1} , respectively. In panel B the decrease of the ratio of

the maleic acid double bond at 1655 cm^{-1} to the C-O bond at 1725 cm^{-1} is shown, which characterizes the course of the copolymerization.

Conclusions

In this paper we discussed recent experimental and theoretical investigations of linear and nonlinear resonance Raman scattering from simple scattering systems as well as on Raman-Mie scattering from optically levitated microparticles.

First, we presented continuum resonance Raman scattering from isotopically pure halogen and interhalogen molecules and reported how the observed spectra can be simulated by applying first principles and numerical calculations based on either the time independent expression or the time dependent approach. It was also shown how this type of scattering can be applied to precisely determine the potential functions of repulsive excited electronic states.

Also, examples of a symmetry principle for corresponding Stokes and anti-Stokes Raman spectra, for a reflection principle and for scattering delay times were given and discussed.

Next, we showed the applicability of linear and especially nonlinear resonance Raman scattering to the investigation of macro molecules. In general, diacetylene (DA) polymer chains show color effects. The simultaneous occurrence of two well-separated color forms (Y and P) in FBS, TS/FBS, and TS6 DA crystals motivated us to investigate the origin of these color zones in detail by applying absorption, luminescence, resonance Raman, and resonance CARS spectroscopy. From the absorption spectra a first interpretation of the color effects was obtained. One result was that the absorption of the Y zone contains different features which can be ascribed to different polymer chains in the DA crystals. We demonstrated that the Y zone contains chains of shorter conjugation lengths than the P zone. Applying resonance Raman spectroscopy we tried to gain more structural information from the Y chains. However, there are limitations to this type of spectroscopy because of the strong luminescence arising from the Y zones. We found that resonance CARS spectroscopy is capable of serving as an excellent alternative spectroscopical method. We gained sufficient information by the nonlinear method to characterize the nature of Y chains far more precisely. We were able to present a plausible model for the origin of color zones. In this model, {111} growth sectors containing edge dislocations act as defects on side groups of DA crystals, and therefore shift the electronic as well as the vibronic energies. The latter is due to the change of the conjugation length of the π electrons in the polymer backbones. In our opinion the disturbance of the planarity of the polymer backbone is the cause of nearly all chromism effects in DA polymers. Although there are several reasons

Figure 22. (A) Time dependence of Raman spectra of the polymerization and copolymerization of styrene (morphology-dependent resonances are marked by asterisks). (B) Intensity ratio of the maleic acid double bonding to the C-O bonding as a function of time.

for such a disturbance, we believe that it is mainly caused by side group geometry effects. This also explains the strong dependence of chromisms on the chemical groups substituted to the DAs.

Finally, we presented an experimental setup which allows the characterization of a single optically levitated microparticle by simultaneous recording of Raman-Mie spectra, Mie scattering data, as well as the laser power required for a stable optical levitation. By applying a developed analysis algorithm based on the Mie theory, we were able to describe particle properties, including droplet size, refractive index, and surface temperature. We showed that the results obtained could be verified by simulation of Raman-Mie spectra or the time dependent radiation pressure. Finally, we showed the application of the experimental techniques developed and the theoretical formalism on complex chemical reactions occurring on the droplet surface or inside the droplet.

Acknowledgments

We very much appreciate collaboration from Drs. M. Ganz and P. Vogt concerning continuum resonance Raman scattering, as well as from Dr. M. Lankers, Dr. I. Hartmann, M. Trunk, E. Urlaub, and J. Musick relating to work in droplet spectroscopy. We thank Professor M. Schwoerer, University of Bayreuth, Germany, for making the DA crystals available to us. Some of the absorption measurements were performed in his laboratory. We are very grateful to Mrs. I. Müller for growing the excellent crystals. Financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie e.V. is gratefully acknowledged.

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